

# SCIENCE FOR GLASS PRODUCTION

UDC 666.113.641':541.184.642/644:620.192.42

## STRUCTURE FORMATION IN PRODUCTION OF YTTRIUM-SILICATE MATERIALS BY THE SOL-GEL METHOD

**P. D. Sarkisov,<sup>1</sup> L. A. Orlova,<sup>1</sup> N. V. Popovich,<sup>1</sup> and Yu. E. Anan'eva<sup>1</sup>**Translated from *Steklo i Keramika*, No. 1, pp. 3–6, January, 2007.

---

Materials made from yttrium silicates were synthesized by the sol-gel method. The effect of the amount of yttrium oxide, which varied from 10 to 50% (molar content), and the water:alcoholate molar ratio was investigated. Structure formation and the character of crystallization of gels in heat treatment in the 650–1300°C range were investigated.

---

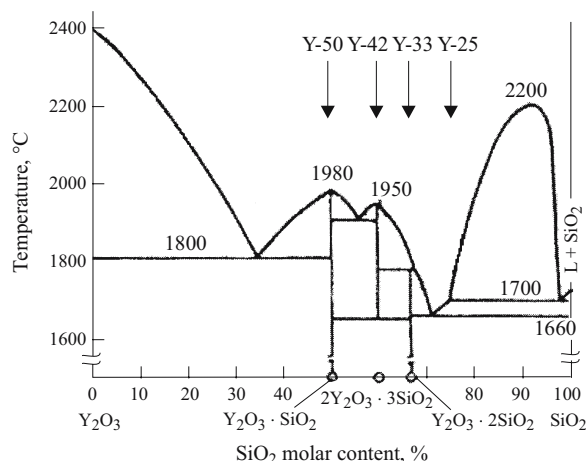
One of the most important trends in modern materials science is the creation of new construction and composite materials. They include silicon carbide composites reinforced with carbon fibres. Such materials are distinguished by high strength characteristics, heat resistance, and low weight, so that they can be used in aviation and aerospace engineering as high-temperature construction materials, for manufacturing parts for gas turbines, diesel engines, and heat exchangers, and in triboengineering [1, 2].

In reducing conditions, silicon carbide composite materials with addition of carbon retain good mechanical properties up to a temperature of 2000, but in oxidizing conditions, their use is limited by possible oxidation of the carbon at temperatures above 400. The creation of new ceramic matrix materials based on high-melting oxide matrices on one hand, and development of high-temperature protective coatings on the other are possible methods of solving this problem. Such materials must satisfy certain requirements; the fundamental ones are: high melting point, steam resistance, low thermal conduction and TCLE values close to the TCLE of silicon carbide. Materials in which silicates and aluminosilicates — mullite, cordierite, strontium and barium aluminosilicates, forsterite, and yttrium silicates are the dominant crystalline phases satisfy these requirements to the greatest degree (US Patent No. 6759151) [3, 4]. These phases are obtained from mixtures of oxides with traditional solid-phase synthesis technologies at temperatures above 1500–1600°C and this requires important power consumption. Interest in new ener-

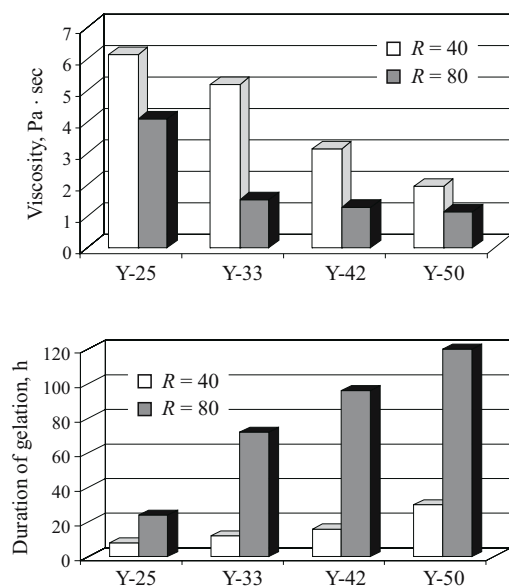
gy-saving technologies, including the sol-gel method, has recently increased. Sol-gel technology is a promising method of obtaining high-temperature materials that allows regulating the structure and properties of the materials by changing the conditions of synthesis.

We investigated sol-gel synthesis by the materials method based on the yttrium-silicate system and the effect of the composition of the solutions on the character of structure formation and crystallization. This system is of interest because yttrium oxyorthosilicate  $Y_2SiO_5$  and pyrosilicate  $Y_2Si_2O_7$ , which have high performance characteristics, are the basic crystalline phases: the melting point of  $Y_2SiO_5$  is 1980°C, the TCLE is  $(22–38) \times 10^{-7} K^{-1}$ , the melting point of  $Y_2Si_2O_7$  is 1775°C, and the TCLE is  $(50–77) \times 10^{-7} K^{-1}$ . According to some data, the TCLE of yttrium silicate can vary from 22 to  $77 \times 10^{-7} K^{-1}$  as a function of the polymorphous modification and  $Y_2SiO_5 : Y_2Si_2O_7$  phase ratio. The high temperature phase ( $X_2$  phase) of yttrium silicate  $Y_2SiO_5$  has a number of advantages, for example, good erosion resistance and oxygen passability at high temperatures and for use in antioxidant protective coatings on SiC supports. However, the values of the TCLE are higher for the  $X_2$  form of  $Y_2SiO_5$  coatings than for the SiC supports, so that microcracks arise along their boundaries. A high percentage content of  $\delta$ - $Y_2Si_2O_7$  is thus necessary for maximally bringing the TCLE in the coatings closer and ensuring their stability. Other favorable effects observed on addition of  $Y_2Si_2O_7$  are the decrease in the synthesis temperature and degree of porosity of the coatings [5, 6].

<sup>1</sup> D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.



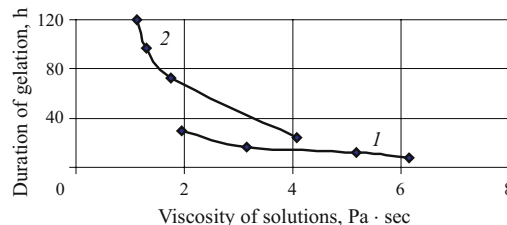
**Fig. 1.** Phase diagram of the  $\text{Y}_2\text{O}_3 - \text{SiO}_2$  system and some of the compositions investigated.



**Fig. 2.** Histogram of the viscosity and duration of gelation as a function of the concentration of yttrium oxide and degree of dilution of the solutions ( $R = \text{H}_2\text{O} : \text{Alk}$ ).

Compositions with a variable yttrium oxide content within the limits of 10 – 50%<sup>2</sup> were selected for the study. The phase diagram of the  $\text{Y}_2\text{O}_3 - \text{SiO}_2$  system [7] and some of the compositions obtained are shown in Fig. 1.

Yttrium oxide and very pure tetraethoxysilane  $\text{Si}(\text{OC}_2\text{H}_5)_4$  (TEOS) were selected as precursors for preparation of the solutions. The solutions also included distilled water, dehydrated ethyl alcohol, and  $\text{HNO}_3$  as a catalyst of hydrolysis. Two series in which the water : silicon alcoholate ratio ( $R = \text{H}_2\text{O} : \text{Alk}$ ) ratio was 40 and 80 were prepared to study the effect of the degree of dilution of the water–alcohol solutions.



**Fig. 3.** Duration of gelation as a function of initial viscosity for a series of solutions with different degrees of dilution: 1)  $R = 40$ ; 2)  $R = 80$ .

In fabrication of different kinds of materials by the sol-gel method (this primarily concerns coatings), the viscosity of the solutions and duration of gelation are the most important process properties. The viscosity of the solutions was determined by capillary viscometry immediately after the solutions were prepared due to their rapid gelation. The duration of gelation was estimated visually by Euler's method — based on the meniscus tilt for 1 min when the beaker with the gel is tilted at a  $45^\circ$  angle. The dependences obtained are shown in Fig. 2.

The composition of the solutions significantly affects the viscosity. With a decrease in the  $\text{Y}_2\text{O}_3$  content in the solution, its viscosity increases markedly — from 1.9 to 6.2 Pa·sec, which is due to an increase in the concentration of TEOS. The mechanism of hydrolysis and polycondensation reactions is greatly dependent on the water : silicon alcoholate ratio. An increase in the ratio of water to alcoholate by 2 times (from  $R = 40$  to  $R = 80$ ) decreases the viscosity of the solutions, slows hydrolysis and polycondensation, and correspondingly, significantly increases the duration of gelation — by approximately 3 – 6 times.

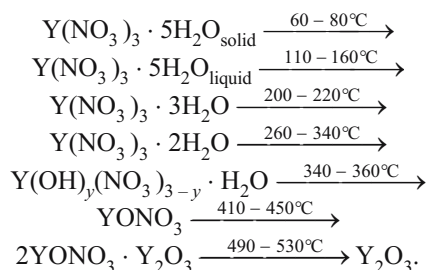
The dependences of the viscosity and duration of gelation for two series of solutions are shown in Fig. 3. Mathematical processing of the experimental data showed that for the first series of compositions ( $R = 40$ ), the dependence is exponential in character, and for the compositions of solutions from the second series ( $R = 80$ ), it is described by a logarithmic function. This suggests that solutions with a high degree of dilution are more promising for making protective yttrium-silicate coatings since they have a broader working viscosity range.

The gels obtained were aged at room temperature for 10 – 20 days. Important shrinkage and cracking of the gels were observed in all compositions during drying. In prolonged aging, needle-shaped white crystals of yttrium nitrate crystal hydrate  $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  formed on the surface in 12 – 15 days.

The thermograms of gels obtained from solutions with different  $\text{Y}_2\text{O}_3$  contents are shown in Fig. 4. Endothermic effects related to elimination of crystal hydrate water and alcohol appeared on all DTA curves in the 40 – 170°C range. A second group of endothermic effects was identified in the 200 – 520°C temperature range. They appeared to the great-

<sup>2</sup> Here and below: molar content.

est degree for the composition with a 50%  $Y_2O_3$  content, and as its concentration decreased, these endothermic effects became slightly blurred and the maxima were shifted to the region of lower temperatures. According to the data in [8], these effects could be due to decomposition of the yttrium nitrate crystal hydrate by stages:



Exothermic effects caused by crystallization of the gels appeared at 1060–1100°C.

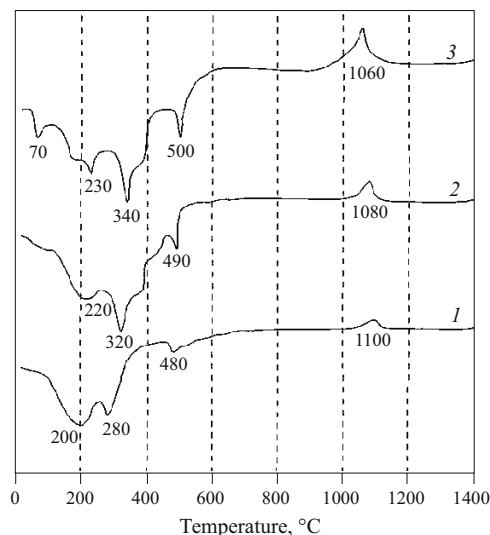
The gels were calcined at 650°C in a silite furnace and held for 0.5 h to totally remove products of hydrolysis and polycondensation. There was an amorphous halo in the x-ray patterns of the calcined gels, and all compositions were totally x-ray-amorphous.

Phase formation was investigated by mass crystallization of the gels in the 900–1300°C temperature range with a 100°C step and holding for 1 h. Crystallization began at 900°C in compositions Y-33 and Y-50 corresponding to the stoichiometric compositions  $Y_2Si_2O_7$  and  $Y_2SiO_5$ , respectively. The structure of the remaining samples was basically amorphous, and the crystalline phase was present in an insignificant amount regardless of the composition. When the heat treatment temperature was increased, the content of amorphous phase in most samples decreased sharply. This was confirmed by the additional decrease in the diffuse region in the diffractograms and the appearance of distinct, intensive lines corresponding to different crystalline phases.

The character of crystallization of gels of the  $Y_2O_3$ – $SiO_2$  system in heat treatment in the 1000–1300°C range is as follows

Composition	Phase
Y-10, Y-20 . . . . .	$\alpha$ - $Y_2Si_2O_7$ $\delta$ - $Y_2Si_2O_7$ Traces of $\alpha$ -cristobalite
Y-29, Y-33 . . . . .	$\alpha$ - $Y_2Si_2O_7$ $\delta$ - $Y_2Si_2O_7$
Y-38 . . . . .	$Y_{4.67}(SiO_4)_3O$
Y-50 . . . . .	$Y_2SiO_5$ ( $X_1$ ) $Y_2SiO_5$ ( $X_2$ ) at temperatures above 1200 °C

Formation of this phase was characteristic of compositions containing 10–20%  $Y_2O_3$  and located in the crystallization field of yttrium pyrosilicate in the 1000–1300°C temperature range. Two polymorphous forms were present: low-temperature  $\alpha$ - $Y_2Si_2O_7$  and high-temperature  $\delta$ - $Y_2Si_2O_7$ . In addition,  $\alpha$ -cristobalite was present in small quantities in

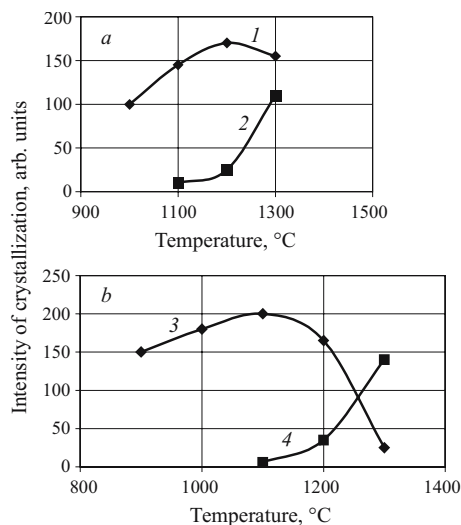


**Fig. 4.** Results of derivatographic analysis of gels: 1, 2, and 3) 10, 33, and 50%  $Y_2O_3$ , respectively.

the samples treated with heat at 1300°C. A single-phase product consisting of the  $\alpha$ - and  $\delta$ -modifications of  $Y_2Si_2O_7$  was formed at a higher  $Y_2O_3$  content, 28.5% (eutectic point on the phase diagram) and 33.3% (stoichiometric composition of yttrium pyrosilicate). The following reflections in the diffractograms correspond to these modifications: 3.01<sub>100</sub>, 2.91<sub>80</sub>, and 2.80<sub>50</sub> Å — for the  $\alpha$ -form of  $Y_2Si_2O_7$  (ASTM 38-0223), and 2.87<sub>100</sub>, 3.08<sub>80</sub>, and 4.07<sub>70</sub> Å — for the  $\delta$ -modification of  $Y_2Si_2O_7$  (ASTM 45-0043). The composition Y-38 crystallized with formation of the  $Y_{4.67}(SiO_4)_3O$  phase characterized by a hexagonal system. According to the phase diagram [7], this composition is close to the compound  $2Y_2O_3 \cdot 3SiO_2$ , which is stable in the 1950–1650°C region. At 1650°C, this compound decomposes with formation of a mixture of two compounds —  $Y_2SiO_5$  and  $Y_2Si_2O_7$ , and the process is reversible.

At the maximum  $Y_2O_3$  content of 50.0% (stoichiometric composition of yttrium oxyorthosilicate), the low-temperature form of  $Y_2SiO_5$  ( $X_1$ ) is formed in the temperature region above 900°C and passes into the dominant high-temperature modification  $Y_2SiO_5$  ( $X_2$ ) in the 1200–1300°C region. The results of a comparative quantitative x-ray-phase analysis of the samples as a function of the heat treatment temperature are shown in Fig. 5 for compositions Y-33 and Y-50. The high-temperature forms of  $Y_2Si_2O_7$  and  $Y_2SiO_5$  appeared at 1100 and 1200°C, respectively. It should be noted that according to the published data, these crystalline phases are formed in the 1400–1600°C temperature range in the traditional method of preparation by solid-phase sintering of oxides. In addition, in solid-phase sintering, reflections of  $Y_2O_3$  are always present in the diffractograms of heat-treated samples, even in compositions with a 50%  $SiO_2$  content, and completion of the reaction is not ensured.

Use of the sol-gel method thus allows significantly reducing the temperature of formation of crystalline phases



**Fig. 5.** Relative content of crystalline phases as a function of heat treatment temperature for compositions containing 33% (a) and 50% (b)  $\text{Y}_2\text{O}_3$ : 1) Low-temperature modification of  $\alpha\text{-Y}_2\text{Si}_2\text{O}_7$ ; 2) high-temperature modification of  $\delta\text{-Y}_2\text{Si}_2\text{O}_7$ ; 3) low-temperature form of  $\text{Y}_2\text{SiO}_5$ ; 4) high-temperature modification of  $\text{Y}_2\text{SiO}_5$ .

and ensures obtaining monophasic products. The materials developed can be used as matrices or antioxidant coatings for ceramic-matrix composites.

## REFERENCES

1. M. E. Westwood, F. H. Hayes, R. J. Day, and R. Taylor, "Oxidation protection of ceramic composites with carbon fibre reinforcement," *J. Mater. Sci.*, **31**, 1389 – 1397 (1996).
2. K. G. Warriar, G. M. Kumar, and S. Ananthakumar, "Densification and mechanical properties of mullite-SiC nanocomposites synthesized through sol-gel coated precursors," *Bull. Mater. Sci.*, **24**(2), 191 – 195 (2001).
3. M. Ferraris, M. Salvo, and F. Smeacetto, "Cordierite – mullite coating for SiC/SiC composites," *J. Eur. Ceram. Soc.*, **22**(13), 2343 – 2347 (2002).
4. J. D. Webster, M. E. Westwood, F. H. Hayes, et al., "Oxidation protection coatings for C/SiC based on yttrium silicate," *J. Eur. Ceram. Soc.*, **18**, 2345 – 2350 (1998).
5. K. Fukuda and H. Matsubara, "Thermal expansion of  $\delta$ -yttrium disilicate," *J. Am. Ceram. Soc.*, **87**(1), 89 – 92 (2004).
6. M. Aparacio and A. Duran, "Yttrium silicate coatings for oxidation protection of carbon-silicon carbide composites," *J. Am. Ceram. Soc.*, **83**(6), 1351 – 1355 (2000).
7. I. A. Toropov, V. P. Barzakovskii, I. A. Bondar', and Yu. P. Udalov, *Phase Diagrams of Silicate Systems. A Handbook* [in Russian], Nauka, Moscow – Leningrad (1965).
8. Simon K. Kh. Del Pino, *Thermal Decomposition and Some Physicochemical Properties of Yttrium Nitrate Crystal Hydrates, Author's Abstract of Candidate's Thesis* [in Russian], Moscow (1981).